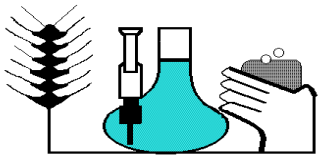
Modified
DRO

Method for Determining Diesel Range Organics

MAINE
HEALTH AND ENVIRONMENTAL TESTING LABORATORY



METHOD 4.1.25
9/06/95

MODIFIED METHOD FOR DETERMINATION OF DIESEL RANGE ORGANICS

1. Scope and Application

1.1 This method is designed to measure the concentration of diesel range organics in water and soil. This corresponds to a hydrocarbon range of C_{10}-C_{28} inclusive and a boiling point range between approximately 170°C and 430°C.

1.2 This method is based on a solvent extraction, Gas Chromatography (GC) procedure. This method should be used by, or under supervision of, analysts experienced in solvent extraction and the use of gas chromatographs. the analysts should be skilled in the interpretation of gas chromatograms and their use as a quantitative tool.

1.3 The method is designed to measure mid-range petroleum products such as diesel (#2 fuel oil) or kerosene (#1 fuel oil). Components greater than C_{28} present in products such as motor oils or lubricating oils are detectable under the conditions of the method. If, based on a review of the chromatogram, the presence of these product types is suspected, a qualitative description should be included in the report. If quantitative results are reported they should be reported as approximate. Additional analyses may be performed including, but not limited to analysis of additional reference materials. These additional efforts are not contained within this method.
Note: The chromatogram must be run through the normal c36 hydrocarbon(n-hexatriacontane).

2. Summary of Method

2.1 This method provides gas chromatographic conditions for the detection of semi-volatile petroleum fractions such as diesel, fuel oil #2, or kerosene. Samples are analyzed utilizing extraction to dissolve the organic constituents. The extract is dried, concentrated and injected into a capillary column gas chromatograph. The gas chromatograph is temperature programmed to facilitate separation of organic compounds. Detection and quantitation is based on FID detector response compared to a diesel component standard using an external standard technique.

2.2 This method is suitable for the analysis of waters, soils, or wastes.

2.3 This method is based in part on 1) PETROLEUM HYDROCARBON METHODS by API revised August 1993; 2) work by the Wisconsin Ad-Hoc Committee on LUST Program Analytical Requirements and Wisconsin State Laboratory of Hygiene; and 3) work by the Maine Hydrocarbon Study Committee.

3. Definitions

3.1 Diesel Range Organics (DRO): All resolved and unresolved material eluting from n-decane (n-C_{10}) through n-octacosane (n-C_{28}), inclusive. Quantitation is based on direct comparison of the area within this range to the total area of the 10 components in the Diesel Component Standard.

3.2 Diesel Component Standard: A ten component blend of typical diesel compounds (Table 1). this standard serves as a quantitation standard and a retention time window for diesel range organics.

3.3 Diesel Component Spike: A reagent water or method blank sample spiked with the Diesel Component Standard and run through the method (including extraction) with samples as a quality control check. See Section 10.2 & 10.3.

3.4 Surrogate Control Sample (Surrogate Blank): A reagent water or soil blank spiked with the surrogate compound and run through the method (including extraction). The surrogate recovery is used as a laboratory control. See Section 7.10.

3.5 Method Detection Limit (MDL): Minimum concentration that an analyte can be measured and reported with a 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte. The MDL is determined using EPA Appendix B to Part 136, CFR 40 Ch. 1 (7-1-94) using the Student t Test. See Section 11.

3.6 Minimum Reporting Level (MRL): Lab reporting level for a commercial diesel fuel oil mixture must be equal to or greater than the MDL and meet the regulatory requirements for fuel oil. See Section 11.

3.7 Temperature Blank(If required by project): A vial of water supplied by the laboratory, treated in the same manner as sample vials and carried along with samples, to determine if proper cooling of samples has been achieved (less than 6°C). A 40 ml or 60 ml vial will be adequate for this purpose.

3.8 Other terms are as defined in SW-846.

4. Interferences

4.1 Other organic compounds including chlorinated hydrocarbons, phenols, and phthalate esters are measurable. As defined in the method, the DRO results include these compounds. Spills of known specific constituents should be analyzed and quantified by a method specific for those compounds. If the chromatogram exhibits the characteristics of gasoline, the DRO results should be reported but flagged with a recommendation for GRO analysis.

4.2 Method interferences are reduced by washing all glassware with hot soapy water and then rinsing it sequentially with tap water, methanol or acetone, and methylene chloride. Method /reagent blanks (Surrogate Control Samples) must be analyzed with each batch to demonstrate that the samples are free from method interferences.

4.3 High purity reagents such as Burdick and Jackson GC methylene chloride or Baker capillary grade methylene chloride must be used to minimize interferences.

4.4 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. Whenever an unusually concentrated sample is encountered, it should be followed by analysis of a solvent blank to check for cross-contamination.

5. Safety Issues

The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. However, each chemical compound should be treated as a potential health hazard. Exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current file of Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of the chemicals specified in this method. A reference file of Material Safety Data Sheets (MSDS) should also be made available to all personnel involved in the chemical analysis.

6. Apparatus and Materials

6.1 Gas Chromatograph

6.1.1 Gas Chromatograph: Analytical system complete with gas chromatograph and all required accessories, including a detector, column supplies, recorder, gases, and syringes. A capillary split/splitless injector operating in the splitless mode is recommended. A data system capable of determining peak areas by integrating from baseline to baseline is required.

6.1.2 Columns

6.1.2.1 Column 1: 30 m x 0.25 mm ID SPB-1, 1.5 micron film thickness(or equivalent).

6.1.2.2 Column 2: 30 m x 0.25 mm ID SPB-5, 1.5 micron film thickness(or equivalent).

6.1.2.3 Other columns may be used. Capillary columns are required. The column must be capable of resolving typical diesel components, and the solvent front from C_{10}. The column must also resolve pristane from C 17 and phytane from C 18 in a commercial diesel fuel oil standard at a level equal to the minimum reporting level.

Peaks are considered to be resolved when 60% resolution has been achieved.

$$\% \text{ RES} = \frac{(\text{height of smallest pk-height of valley}) \times 100\%}{\text{(height of smallest peak)}}$$

6.1.3 Detector: Flame ionization (FID).

6.2 Concentrator tube, Kuderna-Danish: 10 ml graduated (Kontes K-570050-1025 or equivalent).

6.3 Evaporative flask, Kuderna-Danish: Attach to concentrator tube with springs or clips.

6.4 Snyder column, Kuderna-Danish: Rotary evaporation set-up may also be used alternatively. Other concentration apparatus may be used, if equivalency can be demonstrated.

6.5 Nitrogen evaporator with high purity nitrogen gas source.

6.6 Analytical balance: A balance capable of accurately weighing 0.0001 g (for standards). A top-loading balance capable of weighing to the nearest 0.01 g (for soil samples).

6.7 Ultrasonic Cell Disrupter: A horn-type sonicator equipped with a titanium tip should be used. A Heat Systems - Ultrasonics, Inc. Model W-385 (475 Watt) sonicator or equivalent (power wattage must be a minimum of 375 with pulsing capability and No. 200 1/2" Tapped Disrupter Horn) plus No. 207 3/4" Tapped Disrupter Horn, and No. 419 1/8" Standard tapered Microtip probe.

6.8 A Sonabox is recommended with the above disrupter for decreasing sound (Heat Systems-Ultrasonics, Inc., Model 432 13 or equivalent).

6.9 Water bath: Heated with concentric ring cover, capable of temperature control ($\pm$2°C). The bath should be used in a hood.

6.10 VOC Vials and Bottles: 40 ml vials or 60 ml VOC vials with Teflon lined silicone septa or wide mouth with Teflon lined caps for soils (recommend 2 or 4 oz.). Amber 1 liter bottles with Teflon lined caps for waters.

6.11 Separatory funnel : 2000 ml with Teflon stopcock.

6.12 Microsyringes: 1 ul, 5 ul, 10 ul, 25 ul, and 100 ul.

6.13 Disposable pipettes: Pasteur.

6.14 Boiling chips: Approximately 10/40 mesh. Heat to 400°C for 30 minutes or solvent extract with methylene chloride.

6.15 15 ml graduated centrifuge tubes.

6.16 2 ml (and larger) vials with Teflon lined caps for storage of extracts.

6.17 Glass funnels, beakers and/or Erlenmeyer flasks.

6.18 Glass wool, solvent rinsed.

7. Reagents and Standards

7.1 Reagent Water: Organic free water.

7.2 Solvents: Methylene chloride and acetone: Pesticide grade or equivalent. Store away from other solvents.

7.3 Sodium sulfate: (ASC) granular, anhydrous. Purify by heating at 400°C for 4 hours in a shallow tray or solvent extraction with methylene chloride.

7.4 Sodium Chloride: Purify by heating at 400°C for 4 hours in a shallow tray or solvent extracting with methylene chloride.

7.5 Acid for preserving water samples: A 1:1 mixture of reagent water and concentrated hydrochloric acid. Use 5 ml per 1 L sample. Alternatively, add 2 grams of sodium hydrogen sulfate per 1 L sample.

7.6 DRO free sand or soil.

7.7 Stock Standards: Prepare individual stock standards for the diesel components in methylene chloride at approximately 20 mg/ml. Preparation of individual stock standards can be avoided by purchasing a certified mix of the diesel component standard, available through several venders. Note: A DRO standard mix at 2000 ug/ml is available in methylene chloride from Chem Service (CATALOGUE #- TPH-5M.)

7.7.1 Place about 8 mls of solvent in a 10 ml tared ground-glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 min. or until all solvent-wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

7.7.2 Using a 100 ul syringe, immediately add 20-30 ul of the diesel component to the flask; then reweigh. The liquid must fall directly into the solvent without contacting the neck of the flask.

7.7.3 Dilute to volume, stopper, and then mix by inverting the flask three times. Calculate the concentration in micrograms per microliter (ug/ul) from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

7.7.4 Transfer the stock standard solution into a Teflon-sealed screw-cap/crimp cap bottle. Store, with minimal headspace, at 6°C or less and protect from light.

7.7.5 Standards must be replaced after 6 months, or sooner if comparison with check standards indicates a problem.

7.8 Diesel Component Standard: Purchase a certified Diesel Range Organic Component Standard or prepare the standard in methylene chloride at the concentration listed in Table 1.[Note: DRO standards for preparing the Diesel Component Spikes must be prepared in acetone or other suitable water soluble solvent]. These standards should be stored with minimal headspace and should be checked frequently for

signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

7.9 Calibration Standards: Prepare Calibration standards at a minimum of three concentration levels in methylene chloride from the Diesel Component Standard. One of the concentration levels should be at 50 ug/ml. The remaining concentration levels should correspond to the working range of the GC.

7.10 Surrogate Control Standard: The analyst should monitor the method performance by spiking each sample, blank and spiked sample with a surrogate compound. Suggested surrogates are ortho-terphenyl, para-terphenyl or 5-alpha-androstane; the suggested working solution is 20 ug/ml in acetone or other suitable water soluble solvent. **(note: The selection of the surrogate and working concentration may need to be changed depending on the capillary column used and the linear range of the FID detector system. The concentration of the working surrogate standard may be increased to allow for a decreased volume of acetone in the soil samples).**

8. Laboratory Sample and Chain of Custody Handling

8.1 When water or soil samples are not received cold, the fact should be noted on the chain of custody form.

8.2 When water samples are received the pH should be checked with pH paper to ensure that the samples have been acid preserved. If the pH is not < 2, the fact should be noted on the chain of custody form. Samples that have not been preserved should be preserved at this time and a notation made on the chain of custody form.

8.3 Samples are to be placed in a refrigerator at 4°C±2°C as soon as possible after receipt.

8.4 Water samples must be extracted within 7 days and analyzed within 40 days of extraction.

8.5 Soil samples must be extracted within 14 days and analyzed within 40 days of extraction.

9. Procedure

9.1 Samples are analyzed by GC/FID. Waters are extracted using a separatory funnel or continuous liquid liquid extraction technique. Soils are extracted using a sonication extraction technique. Alternatively, soils may be extracted by a Soxhlet extraction technique. Details are given in section 9.5. After the extracts are concentrated, an appropriate volume (usually 2 ul-5 ul)is injected directly into the GC(Recommend using splitless injection techniques). **[Note: NaCl may be added to water samples to improve extraction efficiency].**

9.2 Gas Chromatography

9.2.1 Conditions (For both column 1 and 2): Set column temperature to 40°C for 2 minutes, then 8°C/min. to 280°C and hold for 15 min. Set FID Detector to 300°C and injector to 250°C. Conditions may be altered to improve resolution or recovery of diesel range organics.

9.2.2 Other columns-set GC conditions to meet the criteria in 6.1.2.3.

9.3 Retention Time Window and Quantitation

9.3.1 Diesel Range Organics (DRO): All chromatographic material eluting from n-decane through n-octacosane inclusive. Quantitation is based on direct comparison of the total area within this range including all resolved and unresolved components to the total area of the 10 components in the Diesel Component Standard. (Using a "baseline to baseline" integration as opposed to a "valley to valley" integration.)

9.3.2 The retention time window is defined as beginning approximately .1 minutes before the retention time of n-decane and ending .1 minutes after the retention time of n-octacosane in the calibration run.

9.3.3 The laboratory must determine retention time windows for the first and last standard on each GC column and whenever a new GC column is installed. This data must be retained by the laboratory.

9.3.4 Quantify by summing all resolved and unresolved chromatographic material from n-decane through n-octacosane, inclusive.

9.4 DRO Calibration

9.4.1 Run the Diesel Component Standard at a minimum of three concentration levels at and above the MDL required by this method (50 ug/ml)and covering the linear range of the instrument. Each time a new calibration curve is established the curve should be verified with a standard from an independent source.

Note: 50 ug/ml in the concentrate equals 50 ug/L in the sample when concentrated to 1.0 ml assuming 100% recovery.

9.4.2 Inject each calibration standard. Tabulate the total peak area for the ten components against the mass injected. The results are used to prepare a calibration curve by linear regression or calculate an average response factor.

9.4.3 The working calibration curve must be verified on each working day, and after every 20 samples, by the injection of a calibration standard. If the response for the calibration standard varies from the predicted response by more than 20%, the analytical system should be examined to determine the cause and corrective action should be performed and/or a new

continuing calibration standard should be prepared and analyzed. If the 20% criteria is still not met, the system must be recalibrated. Any samples that were analyzed following standards that did not meet the calibration criteria must be reanalyzed (if reanalysis is not possible, the data must be flagged).

9.5 Sample preparation

9.5.1 Water extraction - Separatory Funnel Liquid-Liquid Extraction

9.5.1.1 Measure a 1-L portion of the sample and transfer to the 2-L separatory funnel. If the sample is in a 1 liter or smaller bottle, mark the water meniscus on the side of the sample bottle for later determination of the sample volume. If the sample is in a larger bottle, use a 1 liter graduated cylinder. Pour the sample into a 2 liter separatory funnel. For blanks and quality control standards, pour 1 liter of reagent water into the separatory funnel. Measure volumes to the nearest 5 ml.

9.5.1.2 Check to make sure the pH is <2. Note on the chain of custody if the pH is not <2.

9.5.1.3 Spike the surrogate solution (prepared in acetone) into the water in the separatory funnel (recommend using 1 ml of 20 ug/ml. Add surrogate to sample in separatory funnel).

Note: Since hydrocarbons tend to separate from water it is important that the spike be injected well under the surface to affect a solution.

9.5.1.4 Add 60 mls methylene chloride to the sample bottle to rinse the inner walls. Transfer the solvent to the separatory funnel. Add 50-55 grams of NaCl to the separatory funnel. After inserting the stopper, gently tilt and rock the funnel to move the salt away from the stop-cock and vent the funnel. Shake the funnel and vent again. Extract the sample by shaking it for two minutes with frequent ventilation. **[Note: Use of NaCl may be considered optional if recoveries and detection limits meet the method requirements.]**

9.5.1.5 Allow the layers to separate. If an emulsion cannot be broken (recovery of <80% of the solvent) transfer the sample, solvent, and emulsion into the extraction chamber of a continuous extractor and proceed as described in 9.5.2. Note: Other means may be useful in breaking the emulsion, such as freezing and centrifuging.

9.5.1.6 Drain the solvent layer into a 250 ml beaker or flask.

9.5.1.7 Repeat the extraction at least once more using a 60 ml aliquot of solvent. Collect the solvent in the same beaker or flask described in 9.5.1.6. Estimate the extract volume. If less than 90 mls is recovered, perform a third extraction.

9.5.1.8 Put a plug of glass wool into a funnel and fill about 2/3 full with Na_2SO_4. Rinse the funnel and Na2SO4 with 30-40 ml methylene chloride, discard. Pour the extract through the Na_2SO_4 into a 500 ml Kuderna-Danish(K-D) evaporative concentrator. (The drying step need not be repeated for soil extracts.) Rinse the beaker and the Na_2SO_4 with small amounts of solvent. Add these rinses to the K-D.

NOTE: Equivalent concentration or drying apparatus may be used.

9.5.1.9 Add a boiling chip to the K-D and attach a Snyder to the top. Pre-wet the column by adding about 1 ml of solvent to the top.

NOTE: The concentration step is critical; losses can occur if care is not taken.

9.5.1.10 Place the K-D in a heated water bath set at a temperature appropriate for the methylene chloride so that the receiver tube is immersed in hot water and the entire lower rounded surface is bathed in steam. When the appropriate volume has been reached(usually 5-7 ml), remove the K-D from the bath and allow it to cool completely.

9.5.1.11 If the extract is highly colored or a precipitate forms during concentration, the final volume should be higher.

9.5.1.12 After the K-D has cooled, rinse the Snyder column and middle flask with a small amount of solvent. Transfer the extract to a calibrated 15 ml centrifuge tube, rinsing with a small amount of solvent. Be sure to rinse all of the ground glass joints well, as compounds collect on the ground glass.

9.5.1.13 Carefully concentrate the extract to 1.0 ml under a gentle stream of nitrogen using an N-evap apparatus or other suitable concentration apparatus. If the extract is highly colored, forms a precipitate, or stops evaporating, the final volume may be higher. Mark the meniscus for final extract volume determination. Transfer the extract to an appropriate sized vial with Teflon lined cap.

9.5.1.14 Record the prep information for the extraction and concentration steps. The sample extract is ready for analysis as in Section 9.5.5.

9.5.2 Water extraction - Continuous Liquid-Liquid Extraction

9.5.2.1 Mount the continuous extractor on appropriate racks.

9.5.2.2 Put 250 ml methylene chloride in a round bottom flask, add a few boiling chips. Add 240 ml of solvent to the extractor flask.

9.5.2.3 Check to make sure that the pH is <2. Note on the chain of custody if the pH is not <2.

9.5.2.4 For samples in 1 liter or smaller bottles, mark the meniscus on the side of the sample bottle for later determination of the sample volume and pour approximately half of the sample into the extractor. When pouring water into the extractor, minimize the disturbance of the solvent layer and avoid getting water into either sidearm by pouring the water down the back of the extractor.

9.5.2.5 Add 50-55 grams of NaCl to the sample remaining in the liter bottle and mix to dissolve the salt. Pour the sample/salt mixture into the extraction funnel. Note: The salt must be dissolved before being put into the extraction flask since it will sink to the bottom of the flask and will not dissolve. For samples in bottles larger than 1 liter, measure 1 liter of the sample in a graduated cylinder. Record the volume to the nearest 5 ml. Dissolve the salt in the sample by mixing in a large flask; or pour the measured sample into the extraction flask, dissolve the salt in reagent grade water and add the solution to the extraction flask. **[Note: Use of NaCl is optional, if the requirements of the quality control section of this method are met].**

9.5.2.6 Spike the working surrogate standard solution (prepared in acetone) into the water (recommend using 1 ml of 20 ug/ml).
Note: Since hydrocarbons tend to separate from water it is important that the spike be made well under the surface to effect a solution.

9.5.2.7 Add 60 ml methylene chloride to the sample bottle to rinse the inner walls. Transfer the solvent to the extraction flask.

9.5.2.8 Add enough reagent water to the extractor flask to allow the solvent in the removable sidearm to just begin to drip into the round bottom flask. Record the total volume of reagent water that was added on the prep sheet.

9.5.2.9 Remove the condenser from the rack and wipe the lower joint and lip with a tissue soaked with solvent. Place the condenser on the top of the extractor. Turn on the cool water supply and check the flow indicators.

9.5.2.10 Turn on the heating mantle. Check after 15 minutes to make sure that the solvent in the round bottom flask is boiling, that solvent is dripping from the lip on the condenser, and that the volume of the solvent in the round bottom flask is still about 240 ml.

9.5.2.11 Check all extractor joints for leaks with a Kimwipe. Allow the extraction to proceed for 18-24 hours.

9.5.2.12 Turn off the heating mantle and allow the apparatus to cool (30-60 minutes) with water flowing through the condenser.

9.5.2.13 The solvent contained in the round bottom flask is the extract. Transfer the extract to a 400 ml beaker, rinsing with a small amount of solvent. If the volume of solvent is less than about 250 ml, record the solvent volume.

9.5.2.14 Go to 9.5.1.8 and proceed with the prep.

9.5.3 Water preparation- disk extraction will be allowed if the quality control requirements of this document can be met.

9.5.4 Soil Preparation-Sonication

9.5.4.1 Mix the sample well to ensure a representative sample. Note any anomalies observed in the sample (presence of foreign materials, variable particle size, presence of oil or aqueous phases, etc.).

9.5.4.2 Until methylene chloride has been added to the soil, the following steps should be performed rapidly to avoid loss of the more volatile extractables. Weigh 25g of the sample into a 250 ml beaker or centrifuge bottle. Add 25g of dried Na_2SO_4 with mixing until the Na_2SO_4/soil mixture is free flowing. If needed, add additional Na_2SO_4.

9.5.4.3 Add 100 ml of methylene chloride to the sample.

9.5.4.4 Spike the surrogate prepared in acetone or other water soluble solvent (recommend using 1 ml of 20 ug/ml) into the methylene chloride/soil mixture. Mix the sample immediately.

9.5.4.5 Sonicate the samples for 2 minutes at an output setting of 10 with the 3/4 inch sonicator horn 1/2 inch below the surface of the solvent (the horn tip should be just above the sediment layer). The sonicator should be in the 1 second pulse mode, with the duty cycle set at 50%.

9.5.4.6 Let soil settle and decant extract into a beaker or flask. Soil/extract mixtures containing fine particulates may need to be centrifuged or decanted or filtered using vacuum or pressure filtration to remove suspended materials.

9.5.4.7 Repeat the extraction twice more using 100 ml aliquots of methylene chloride each time. Collect these extracts in the same beaker or flask described in 9.5.4.7

9.5.4.8 If the extract is not being concentrated (as may be the case in high level samples), record the total volume of the solvent that is recovered. If the extract needs to be concentrated, proceed to 9.5.4.9.

9.5.4.9 Go to 9.5.1.8 and proceed with the prep.

9.5.5 Inject an appropriate volume of concentrated extract into the GC and proceed with the analysis. If the sample concentration exceeds the calibration range for DRO an appropriate dilution should be used. An appropriate dilution is one that keeps the response of major constituents (previously saturated peaks) in the linear range of the detector. If an initial dilution does not accomplish this then an intermediate dilution should be performed.

9.6 Calculations

9.6.1 DRO Calculation: The concentration of Diesel Range Organics in the sample is determined from a summation of the total peak area of all resolved and unresolved chromatographic material eluting from n-decane through n-octacosane, inclusive, using the calibration curve. (Using a "baseline to baseline" integration as opposed to a "valley to valley" integration.) Refer to Section 9.3 (Retention Time Windows and Quantification).

Quantification may be based on average response from the calibration curve or on a linear regression equation derived from the curve. Most labs will probably use the computer software provided with the GC to perform these calculations.
Linear Regression:
From linear regression of calibration standard GC responses (R) against their known concentrations (C in ug/ml) , the following linear equation may be derived[R is plotted on the Y axis; C is plotted on the x axis]:

$R = mC + b$ which can be rearranged to $C = (R-b)/m$

Using the slope (m) and the intercept (b) from this equation the concentration of the sample can be calculated from the following equations:

<u>Water Samples</u>

$$C = [(R_S - b)(V_E)(D)]/[(V_S)(m)]$$

<u>Soil Samples</u>

$$C = [(R_S - b)(V_E)(D)]/[(W)(m)]$$

Where:

C = Concentration of sample in ug/L for waters and mg/kg on a dry weight basis for soils

m = slope of the calibration curve

R_S = GC response of sample in the DRO retention time window

b = intercept of calibration curve

V_E = total volume of sample extract (after concentration) in ml

V_S = volume of water sample in liters

D = dilution factor if water or soil extract was diluted

W = total dry weight of soil sample in gm (wet weight if required by project).

9.6.2 Extraction blank areas cannot be subtracted from the sample areas. Baseline correction is allowed to correct for rises due to temperature programming. A methylene chloride blank may be run to determine the area generated by the baseline bleed. If a solvent blank or extraction blank is above the reporting level all associated samples with ambiguous data must be re-extracted and reanalyzed.

9.6.3 If there are significant peaks or envelopes outside the DRO window the material should be reported qualitatively and/or the results should be calculated using the DRO component standard and reported as approximate. The analyst may wish to calculate the results against a more appropriate standard to give better results.
Note: The sample extracts must be chromatographed through the normal hydrocarbon C36.

9.6.4 All area detected in the DRO window must be reported as "DRO". If the chromatogram exhibits the characteristics of gasoline, the results should be flagged with a recommendation for GRO analysis.

10. Quality Control

10.1 The analyst must make an initial demonstration of the ability to generate acceptable accuracy and precision with this method by successful analysis of the following:

10.1.1 Replicate commercial diesel oil spikes in water: Analysis of at least 7 replicates at a concentration of 100 ug/L (in water) with accuracy of the replicates falling between 60% to 140% of the known concentration. The precision of all replicates should be within 20%.

10.1.2 Replicate commercial diesel oil spikes in soil: Analysis of at least 7 replicates at a concentration of 10 mg/kg with the accuracy of the replicates

falling between 60% and 140% of the known concentration. The precision of all the replicates should be within 20%. Soil spikes should be prepared and analyzed as described in section 10.3 .

10.2 For every 20 water samples analyzed, the lab must analyze a set of duplicate diesel component spikes in reagent water. The Duplicate spikes must be run through the method in the same manner as samples. The accuracy the two water spikes should fall between 60% to 140% of the known concentration with a relative % difference of 20% or less. **Alternatively duplicate samples and spiked samples can be substituted for the laboratory spiked duplicates at a frequency of 10%. Care must be taken to ensure that the samples are homogeneous before analyzing duplicates and spikes.**

10.3 For every 20 soil samples analyzed, the lab must analyze a set of duplicate Diesel Component Spikes in clean sand or soil. The duplicate spikes must be run through the method in the same manner as samples. The accuracy of the two soil spikes should fall between 60% and 140% of the known concentration and the relative % difference should be 20% or less.

Soil spikes are prepared by spiking 25 grams of clean soil or sand with the component standard in methylene chloride (the use 1 ml of a standard at a concentration of 500 ug/ml [50 ug/ml each component] is recommended). The component standard spike should be added at the same step as the surrogate standard, Section 9.5.4.4.

Alternatively duplicate samples and spiked samples can be substituted or the laboratory spiked duplicates at a frequency of 10%. Care just be taken to ensure that the samples are homogeneous before analyzing duplicates and spikes.

10.4 A Surrogate Control Sample (Method Blank) must be extracted and analyzed with each batch of water or soil samples extracted. The amount of material in the blank should not exceed the minimum reporting level.

10.5 Calibration requirements:

10.5.1 When linear regression analysis is used for calculations the correlation coefficient must be at least 0.99.

10.5.2 When average Rf is used for calculations the standard deviations of the Rfs must not exceed 20%.

10.5.3 A Quality Control Check Standard (obtained from a source independent of the calibration standards) should be analyzed concurrent with the calibration standards in order to confirm the validity of the calibration curve. The QC check should fall within 20% of the expected value using the calibration data.

10.5.4 The calibration curve must be verified with each analytical sequence by running a mid-point calibration standard. The response must fall within 20% of the expected response.

10.6 Each analytical sequence should end with a demonstration that the resolution criteria have been met for all samples run in that sequence,i.e., the system should resolve pristane from C17 and phytane from C18 at 50 ug/ml total commercial diesel fuel oil, or at

the minimum reporting level, if lower. In order to minimize the number of rechecks of analyses not meeting resolution requirements, it is suggested that 50 ug/ml commercial diesel fuel oil standards be run after the continuing calibration standard and interspersed periodically in a sequence. Note: Monitoring the resolution of a mid-point commercial diesel fuel oil standard will not satisfy resolution requirements.

10.7 It is recommended that the resolution standard in 10.6 be quantitated periodically against the component standard to monitor for low level recovery of a typical fuel oil product. Expected recovery is 60%-140%.

10.8 If any of the criteria above are not met, the problem must be corrected before further samples are analyzed. Any samples run between the last QC samples that meet the criteria and those that have fallen out should be rerun. If this is not possible, that data must be flagged.

10.9 Laboratory spiked duplicates prepared by spiking fuel oil into blank water in must be run at a minimum frequency of 5%.

Alternatively duplicate samples and spiked samples can be substituted for the laboratory spiked duplicates at a frequency of 10%. Care must be taken to ensure that the samples are homogeneous before analyzing duplicates and spikes.

10.10 Trip blanks, field blanks, field duplicates, matrix spikes and/or temperature blanks may be recommended or required for specific sampling programs.

10.11 Methylene chloride blanks should be run after samples suspected of being highly concentrated to prevent carryover.

10.12 It is recommended that an acceptance criteria be established for recoveries of surrogates. Collect recoveries from 30 samples where no interference is suspected and calculate the mean recovery (X) and standard deviation (S). The acceptance limits for samples not exhibiting matrix interference will be X-3S to X+3S. The warning limits will be X-2S to X+2S. Plotting the surrogate recoveries on a control chart will make checking recoveries easier and is highly recommended.

In samples containing DRO, the surrogate peak may need to be "skimmed" off of an envelope of unresolved material in order to get an accurate peak area. If surrogate recovery is outside of the established limits, verify calculations, dilutions, and standard solutions. Verify instrument performance. Low recovery may be due to sample matrix. The analysis should be repeated to confirm matrix problems if the surrogate recovery is less than 50% or, if the analysis cannot be repeated, the data should be flagged.

High recoveries may be due to co-eluting matrix interference. Surrogate recoveries may be reported as "masked" in high level samples exhibiting matrix interference. Additionally, the surrogate may be reported as "diluted out" in high level water or soil samples that must be diluted for analysis. These samples do not need to be rerun solely to try to bring surrogate recovery into acceptance limits.

10.13 It is highly recommended that gasoline, diesel (#2 fuel oil), kerosene (#1 fuel oil), motor oil or other petroleum products be run

on a periodic basis for identification purposes, at a minimum with each new column and following any significant retention time changes.

11. Method Performance

11.1 Detection limit for waters:

The laboratory must be able to achieve a detection limit of 50 ug/L using a commercial diesel fuel oil mixture spiked into laboratory blank water and calculated against the DRO component standard.

11.2 Detection limit for soils:

The laboratory must be able to achieve a detection limit of 5.0 mg/kg for a commercial diesel fuel oil mixture spiked into blank sand and calculated against the DRO component standard.

12. References

12.1 ASTM "Standards Methods for Comparison of Waterborne Petroleum Oils by Gas Chromatography," 3328-78.

12.2 Wisconsin DNR Modified DRO method, July 1993, Revision 6.

12.3 USEPA SW 846, 3rd edition, Methods 8000, 8100, 3500, 3510, 3520 and 3550.

TABLE I

DIESEL COMPONENT STANDARD AND CONCENTRATIONS

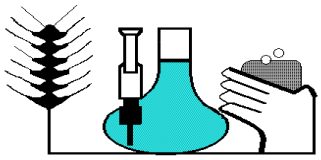
Component	Concentration, ug/ml
Decane	1000
Dodecane	1000
Tetradecane	1000
Hexadecane	1000
Octadecane	1000
Eicosane	1000
Docosane	1000
Tetracosane	1000
Hexacosane	1000
Octacosane	1000
Total	10000

Modified

G R O

Method for Determining Gasoline Range Organics

MAINE
HEALTH AND ENVIRONMENTAL TESTING LABORATORY



METHOD 4.2.17

9/06/95

MODIFIED METHOD FOR DETERMINATION OF GASOLINE RANGE ORGANICS

1. Scope and Application

1.1 This method is designed to measure the concentration of gasoline range organics in water and soil. This procedure measures compounds from MTBE through naphthalene inclusive. This corresponds to a boiling point range between approximately 60°C and 220°C.

1.2 The analytical procedure is based on a purge-and-trap, Gas Chromatography (GC) procedure. The method should be used by, or under the supervision of, analysts experienced in the use of purge-and-trap systems and gas chromatographs. The analysts should be skilled in the interpretation of gas chromatograms and their use as a quantitative tool.

1.3 With the optional PID/FID in series, the method can be extended for the specific determination of petroleum volatile organic compounds (PVOCs) as specified in the current edition of EPA Method 8020.

1.4 See section 11 for method performance criteria.

2. Summary of Method

2.1 The method provides gas chromatographic conditions for the detection of volatile petroleum fractions such as gasoline, Stoddard solvent, or mineral spirits. Samples are analyzed utilizing purge-and-trap sample concentration. The gas chromatograph is temperature programmed and utilizes a capillary column to facilitate separation of organic compounds. Detection is achieved by a flame ionization detector (FID) or FID with photoionization detector (PID) in series (photoionization detector first in the series). Quantitation is based on FID detector response to a gasoline component standard utilizing an external standard method.

2.2 The method is suitable for the analysis of waters, soils, or wastes. Water samples can be analyzed directly for gasoline range organics by purge-and-trap extraction and gas chromatography. Soil or waste samples are dispersed in methanol to dissolve the volatile organic constituents. A portion of the methanolic solution is then analyzed by purge-and-trap GC.

2.3 Soil core samples may be collected in wide mouth jars when field preservation isn't required. Minimum handling is required to reduce VOC loss. Samples that are preserved in the field should be collected in septum vials (60 ml wide mouth vials are recommended).

2.4 Water samples should be collected in 40 ml septum vials and acid preserved when collected.

2.5 This method is based in part on 1) API's PETROLEUM HYDROCARBON METHODS [Revised August 1993], 2) work by the Wisconsin Ad-Hoc Committee on LUST Program Analytical Requirements and Wisconsin State Laboratory of Hygiene; and 3)work by the Maine Laboratory Hydrocarbon Study Committee.

3. Definitions

3.1 Gasoline Range Organics (GRO): All chromatographic peaks eluting from methyl-tertiary-butylether through naphthalene, inclusive. Quantitation is based on a direct comparison of the area within this range to the total area of the 10 components in the Gasoline Component Standard.

3.2 Gasoline Component Standard: A ten component blend of typical gasoline compounds (Table 2). This standard serves as a quantitation standard and a retention time window for gasoline range organics.

3.3 Gasoline Component Spike: A reagent water or method blank sample spiked with the Gasoline Component Standard and run through the method with samples as a quality control check. See Section 10.

3.4 Method Detection Limit (MDL): Minimum concentration that an analyte can be measured and reported with a 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte. The MDL is determined using EPA Appendix B to Part 136, CFR 40 Ch. 1 (7-1-94) using the Student t Test. See Section 11.

3.5 Minimum Reporting Level (MRL): The minimum reporting level for gasoline must be 10 ug/L or less. See Section 11.

3.6 Temperature Blank: (If required by project) A vial of water supplied by the laboratory, treated in the same manner as sample vials and carried along with samples, to determine if proper cooling of samples has been achieved (0°C-6°C). A 40 ml or 60 ml vial will be adequate for this purpose.

3.7 Other terms are as defined in SW-846.

4. Interferences

4.1 Heavier petroleum products such as diesel fuel may contain some volatile components producing a response within the retention time range for GRO. Other compounds that respond to the FID such as chlorinated and oxygenated hydrocarbons are detected by this method and will be included in the concentration. If the analyst suspects that compounds are present that are not present in gasoline mixtures, the analyst should suggest additional analysis. Spills of known specific constituents should be analyzed and quantified by a method specific for those constituents. If the chromatogram exhibits the characteristics of fuel oil, the GRO should be reported but flagged with a recommendation for DRO analysis.

4.2 Samples can become contaminated by diffusion of volatile organics through the sample container septum during shipment and storage or by dissolution of volatiles into the methanol used for preservation. Trip blanks prepared from both reagent water and methanol should be carried through sampling and subsequent storage and handling to serve as a check on such contamination. (Methanol trip blank required only if soil samples are preserved with methanol in the field.)

4.3 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe and/or purging device must be rinsed between samples with reagent water or solvent. For volatile samples containing high concentrations of water-soluble materials, suspended solids, high boiling compounds or organohalides, it may be necessary to wash the syringe or purging device with a detergent solution, rinse with distilled water, and then dry in a 105°C oven between analyses. The trap and other parts of the system are also subject to contamination, therefore, frequent bake-out and purging of the entire system may be required. A screening step is recommended to protect analytical instrumentation. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of a water blank to check for cross-contamination.

4.4 The retention time window definition (methyl-tertiary-butylether through naphthalene inclusive) introduces a negative bias, however, it improves comparability between laboratory data. Note that gasoline blends often contain 10% ethanol which could be responsible for a portion of this negative bias.

5. Safety Issues

The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. However, each chemical compound should be treated as a potential health hazard. Exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets should also be made available to all personnel involved in the chemical analysis.

6. Apparatus and Materials

6.1 Gas Chromatograph

6.1.1 Gas Chromatograph: Analytical system complete with gas chromatograph suitable for purge-and-trap sample introduction and all required accessories, including detectors, column supplies, recorder, gases and syringes. A data system capable of determining peak areas by integrating from baseline to baseline is required.

6.1.2 Columns (Capillary Columns are Required):

6.1.2.1 The capillary column must be capable of resolving typical gasoline components. It must be capable of achieving a 60% resolution of all 10 components, with the exception of meta and para-xylene. It must also be capable of separating methyl-tertiary-butylether from methanol at the concentration resulting from preparation of the standard or in the sample spiked with surrogate. The Resolution is defined as

$$\frac{\text{(Height of Smaller Peak)} - \text{(Height of Valley)}}{\text{(Height of Smaller Peak)}} \times 100\ \%$$

6.1.2.2 Suggested columns: Note either column can be used for soil or water provided the resolution meets the criteria given above.

(1) DB5 60 meter .53 mm ID, 1.5 um film thickness (or equivalent).

(2) Vocol 105 meter .53 mm ID, 3.0 um film thickness (or equivalent).

(3) Any capillary column phase and length and diameter may be used as long as the requirements of resolution of this method are met.

6.1.3 Detector: Flame ionization (FID), or FID in series with a Photoionization detector (PID).

6.1.4 Purge-and-trap device: The purge-and-trap device consists of three separate pieces of equipment: the sample purger, the trap, and the desorber. Several complete devices are commercially available.

6.1.4.1 Commercially available automated sample purge devices may be used, provided that equivalent performance is demonstrated.

6.1.4.2 The recommended trap uses 7.6 cm Carbopack B and 1.3 cm Carbosieve S-III. See Table 1 at end of method for recommended trap conditions.

The Trap length and packing materials may be varied as long as equivalent performance compared to the recommended trap has been verified. Demonstration of equivalency of trap performance must be based on a full range of gasoline components, not just on the 10 components in the standard.

6.1.4.3 Traps should be conditioned, desorbed, and baked according to the manufacturers guidelines. The trap may be vented to the analytical column during daily conditioning, however, the column must be run through the temperature program prior to analysis of samples.

6.1.4.4 The desorber should be capable of rapidly heating the trap to the recommended desorption temperature.

6.2 Analytical balance: A balance capable of accurately weighing 0.0001 g (for preparing standards). A top-loading balance capable of weighing to the nearest 0.01 g (for weighing soil samples).

6.3 Ultrasonic bath.

6.4 VOC Vials: VOC vials with Teflon/silicone septa for soils (60 ml wide mouth vials recommended) and 40 ml VOC vials with Teflon/silicone septa for waters. Soils not preserved in the field may be collected in wide mouth jars with Teflon lined caps (2 or 4 oz jars recommended).

6.5 Syringes: 5 ml gas-tight syringe with shutoff valve.

6.6 Syringe valve: Two-way, with luer ends.

6.7 Volumetric flask (class A): 10 ml, 50 ml, 100 ml, 500 ml, and 1,000 ml with a ground-glass or screw-top stopper.

6.8 Microsyringes: 1 ul, 5 ul, 10 ul, 25 ul, 100 ul, 250 ul, 500 ul, and 1,000 ul.

6.9 Disposable pipettes: Pasteur.

6.10 Spatula: Stainless steel.

6.11 Vials with Teflon lined caps for storage of soil extracts (recommend 2 ml).

6.12 20 ml or 40 ml VOA vials or scintillation vials with Teflon lined septa or caps for soil extractions performed in the lab.

7. Reagents and Standards

7.1 Reagent Water: Organic free water

7.2 Methanol: Purge and trap grade or equivalent. Store away from other solvents.

7.3 Acid for preserving water samples: A 1:1 mixture of reagent water and concentrated hydrochloric acid. Use 2 or more drops per 40 ml VOA vial. Acid may be added to the sample at the time of collection or may be added to the vial prior to the collection. Alternatively add

0.1g of sodium hydrogen sulfate to the empty VOA vial. The final pH of the water should be <2.

7.4 GRO free sand or soil

7.5 Stock Standards: Purchase individual certified component standards or prepare stock standards in methanol using volumetric glassware and appropriate analytical techniques. A concentration of 20 mg/ml is recommended for individual component standards.

7.5.1 Transfer the stock standard solution into a Teflon-sealed screw-cap or crimp cap bottle. Refrigerate, with minimal headspace and protect from light.

7.5.2 Standards must be replaced after 6 months, or sooner if comparison with check standards indicates a problem.

7.6 Gasoline Component Standard: Purchase a certified Gasoline Component Standard or prepare the Gasoline Component Standard at the concentrations shown in Table 2. These standards should be stored with minimal headspace and should be checked frequently for signs of degradation or evaporation. The component standard must be replaced after 6 months or sooner if comparison with a check standard indicates a problem.

7.7 Calibration Standards: Prepare Calibration standards at a minimum of three concentration levels in reagent water from the Gasoline Component Standard. One of the concentration levels should be at the minimum reporting level. The remaining concentration levels should correspond to the working range of the GC system.

7.8 Surrogate Control Standard (SCS): The analyst should monitor the performance of the analytical system by spiking each water sample, standard, water blank and diluted soil extract with a surrogate compound. Bromofluorobenzene and the use of a 5 ul spike of a 20 ug/ml standard is recommended (to give a final concentration of 20 ug/L Bromofluorobenzene). In order to monitor the effectiveness of the method in dealing with each soil matrix, a second surrogate standard should be added to soil samples during the extraction step. Trifluorotoluene and the use of a one point spike at 1.0 ug/ml in the extract is recommended (to give a concentration of 20 ug/L when 100 ul of extract is spiked into 4.9 ml of water).

8. Laboratory Sample Handling and Chain of Custody Documentation.

8.1 Water samples

8.1.1 Water samples should be checked for air bubble (s) and rejected if the bubble(s) are significant.

8.1.2 If samples are not received cold, the fact should be noted on the chain of custody.

8.1.3 The samples are to be placed in a refrigerator at 4°C ± 2°C as soon as possible after they are received at the lab.

8.1.4 A water trip blank that accompanies all samples and is analyzed with the samples may be required for specific projects.

8.1.5 Water samples must be analyzed within 14 days of collection.

8.2 Soil Samples

8.2.1 Note on the chain of custody when samples are not preserved in the field . If the sample is not preserved in the field, the container should be filled to minimize the headspace. If there is a large headspace, this fact should also be noted on the chain of custody.

8.2.2 If samples are not received cold, the fact should be noted on the chain of custody form.

8.2.3 Samples should be refrigerated at (4°C ± 2°C) as soon as possible after they are received at the lab.

8.2.4 Samples that have not been preserved in the field should be preserved in the lab as soon as possible after arrival in the lab. Date and time of preservation should be noted on the chain of custody or on the report. Analysis must be completed within 14 days of collection.

9. Procedure

9.1 Volatile compounds are introduced into the gas chromatograph by purge-and-trap. Purge-and-trap may be used directly on groundwater samples. Soils and solids should be analyzed by methanol extraction followed by purge and trap. Soil concentrations will be reported on a dry weight basis unless specified by the sampler and the results shall indicate whether results are on a wet or dry weight basis. The procedure for determination of dry weight can be found in EPA method 5030, section 7.3.3.1.5.

NOTE: It is highly recommended that all samples be screened prior to analysis. This screening step may be analysis of a solid sample's methanol extract (diluted), the headspace method (SW-846 method 3810), or the hexadecane extraction and screening method (SW-846 Method 3820) or any other screening method.

9.2 Gas Chromatography

9.2.1 Conditions for Column 1: Suggested conditions for a 30 m x 0.53 mm I.D. DB 5, or equivalent: Set helium column pressure as recommended by the manufacturer. Set column temperature to 35°C for 3 min, then 4°C/min to 85°C (hold 1 min), then 8°C/min to 220°C (hold 1 min.), then 20°C/min to 250°C (hold 0. min). Conditions may be altered to improve resolution of gasoline range organics.

9.2.2 Conditions for Column 2: Suggested conditions for a 105 m x 0.53 mm I.D. VOCOL, or equivalent: Set helium column pressure as recommended by the manufacturer. Set column temperature to 35°C for 3.0 min, then 8°C/min to 245°C (hold for 1.0 min). Conditions may be altered to improve resolution of gasoline range organics.

9.2.3 Other columns: Set GC conditions to meet the criteria in 6.1.2.

9.3 Retention Time Window and Quantitation

9.3.1 Gasoline Range Organics (GRO): All chromatographic peaks eluting from methyl-tertiary-butylether through naphthalene, inclusive. Quantitation is based on a direct comparison of the area within this range to the total area of the 10 components in the Gasoline Component Standard. (Using a "baseline to baseline" integration as opposed to a "valley to valley" integration.)

Note: The area of the MTBE peak may be determined by tangent skimming when necessary.

9.3.2 The retention time window is defined as beginning approximately .1 minutes before the retention time of methyl-tertiary-butylether and ending .1 minutes after the retention time of naphthalene in the calibration run.

9.3.3 The laboratory must determine retention time windows for the first and last standard on each GC column and whenever a new GC column is installed. This data must be retained by the laboratory.

9.3.4 Quantify by summing all peak areas eluting from methyl-tertiary-butylether through naphthalene, inclusive.

9.4 GRO Calibration:

9.4.1 Run the Gasoline Component Standard at a minimum of three concentration levels at the minimum reporting level and covering the working range of the instrument. When the calibration curve is run an independent check standard should also be run to validate the curve.

Note: Additional low points may be necessary for the optional PID quantitation.

9.4.2 Follow steps 9.4.2 and 9.4.3 for non automated systems. Skip to 9.4.4 for automated systems.

Prepare final solutions containing required concentrations of calibration standards from the Gasoline Component Standard directly in the 5 ml glass syringe as follows:

9.4.2.1. Add the aliquot of calibration solution directly to the reagent water in the glass syringe by inserting the needle through the syringe end.

9.4.2.2. When discharging the contents of the microsyringe, be sure that the end of the syringe needle is well beneath the surface of the reagent water.

9.4.2.3. Inject the standard into the purge vessel through the two way valve.

9.4.3 Inject 5 mls of each calibration standard utilizing the purge-and-trap analysis outlined in 9.5.1.9-9.5.1.12. Tabulate the entire peak area (baseline to baseline) for the ten components against the mass injected. The results are used to prepare a calibration curve by linear regression or to calculate the average response for calibration purposes.

9.4.4 For automated systems follow the manufacturer’s recommended procedures.

9.4.5 The working calibration curve must be verified on each working day, by the injection of a mid-point Gasoline Component Standard. If the response for the Gasoline Component Standard varies from the predicted response by more than 20%, the analytical system should be examined to determine the cause and corrective action should be performed and/or a new continuing calibration standard should be prepared and analyzed. If the 20% criteria is still not met, the system must be recalibrated. Any samples that were analyzed following standards that did not meet calibration criteria must be reanalyzed (if reanalysis is not possible, the data must be flagged).

9.5 Gas Chromatographic Analysis:

9.5.1 Water Samples: Introduce volatile compounds into the gas chromatograph using the purge-and-trap method. For automated systems follow the manufacturer's recommended procedure.

9.5.1.1 Adjust the purge gas flow rate (nitrogen or helium) to 25-40 ml/min on the purge-and-trap device.

9.5.1.2 Remove the plunger from a 5 ml gas-tight syringe. Open the sample or standard bottle and carefully pour the sample into the syringe. Replace the plunger and vent any residual air while adjusting the sample volume to 5.0 ml. This process of taking an aliquot destroys the validity of the liquid sample for future analysis; therefore, if there is only one 40 ml vial, the analyst should fill a second syringe (equipped with a syringe valve) at this time to protect against possible loss of sample integrity. This second sample is stored at 4°C and maintained only until such time when the analyst has determined that the first sample has been analyzed properly. Care must be taken to prevent air from leaking into the syringe.

9.5.1.3 The following procedure is appropriate for diluting purgeable samples. All steps must be performed without delays until the diluted sample is in a gas-tight syringe.

9.5.1.4 Dilutions may be made in volumetric flasks (10 ml to 100 ml). Select the volumetric flask that will allow for the necessary dilution. Intermediate dilutions may be necessary for highly concentrated samples.

9.5.1.5 Calculate the approximate volume of reagent water to be added to the volumetric flask selected and add slightly less than this volume of reagent water to the flask.

9.5.1.6 Inject the proper aliquot of samples (taken from a filled VOA vial or from a storage syringe prepared as in Paragraph 9.5.1.2) into the flask. If aliquots of less than 1 ml are required, use microliter syringes and deep injections to transfer the sample aliquot to the flask. Dilute the sample to the mark with reagent water. Cap the flask and invert three times. Repeat the above procedure for additional dilutions. Alternatively the dilutions can be made directly in a gas tight syringe to avoid further loss of volatiles.

9.5.1.7 Fill a 5 ml syringe with diluted sample as in Paragraph 9.5.1.2.

9.5.1.8 Add surrogate to sample or diluted sample by spiking the surrogate standard directly into the syringe. Inject sample into the purging chamber.

9.5.1.9 Close the valve and purge the sample for 11 minutes at ambient temperature.

9.5.1.10 At the conclusion of the purge time, attach the trap to the chromatograph, adjust the device to the desorb mode, and begin the gas chromatographic temperature program and GC data acquisition. Concurrently, introduce the trapped materials to the gas chromatographic column by rapidly heating the trap to the manufacturer's recommended desorption temperature and backflushing the trap for the recommended desorption time.

9.5.1.11 While the trap is desorbing into the gas chromatograph, empty the purging chamber. Wash the chamber with a minimum of two 5 ml flushes of reagent water (or methanol followed by reagent water) to avoid carryover of pollutant compounds into subsequent analyses.

9.5.1.12 After desorbing the sample, recondition the trap by returning the purge-and-trap device to the purge mode. Wait 15 sec; then close the syringe valve on the purging device to begin gas flow through the trap. The trap temperature should be maintained at the recommended bake temperature. After approximately 7-35 min, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When cool, the trap is ready for the next sample.

9.5.1.13 If the initial analysis of a sample or a dilution of the sample has a concentration of analytes that exceeds the initial calibration range, the sample must be reanalyzed at a higher dilution. When a sample is analyzed that has a saturated response from a compound, this analysis must be followed by a blank reagent water analysis. If the blank analysis is not free of interferences, the system must be decontaminated. Sample analysis may not resume until a blank can be analyzed that is free of interferences.

9.5.1.14 All dilutions should keep the response of the major constituents (previously saturated peaks) in the linear range of the curve.

9.5.1.15 All water samples should be checked to make sure that they were preserved. After sample analysis (or after removing an aliquot for analysis), check the pH of

the water using pH paper. If the pH is not <2, this fact should be noted on the chain of custody form.

9.5.2 Methanol Extraction for Soil/Sediment: This method is based on extracting the sediment/soil with methanol. An aliquot of the extract is added to reagent water and purged at the conditions indicated in Table 1. A screening analysis is recommended (see 9.1).

9.5.2.1 Add approximately 10 gms sample into a tared sample vial and weigh to the nearest .01 gm. Immediately add 10 mls of methanol to the vial. Spike the sample by syringing the surrogate trifluorotoluene into the methanol. Alternatively, the surrogate can be added to the methanol prior to the addition of the methanol to the soil.

If the soil sample has been methanol preserved in the field, both the weight of the soil and the volume of the methanol must be recorded. The ratio of the soil to methanol should be approximately 1 gram soil : 1 milliliter of methanol with a minimum soil weight of 10 grams.

The addition of trifluorotoluene is not required for samples that have been preserved in the field.

9.5.2.2 Shake the sample for 2 minutes and sonicate for 20 minutes.

9.5.2.3 Allow sediment to settle until a layer of methanol is apparent. Centrifuge if necessary. Transfer an aliquot of the extract to a small vial with a Teflon lined cap for storage, using a Pasteur pipette and leaving a small amount of headspace in the archive vial. If not analyzed immediately store at 6°C or less.

9.5.2.4 Using a microliter syringe, withdraw an appropriate volume.

9.5.2.5 Remove the plunger from a 5.0 ml gas tight syringe equipped with a syringe valve and fill until overflowing with reagent water. Replace the plunger and compress the water to vent trapped air. Adjust the volume to allow for addition of the extract (for 100 ul of extract adjust to 4.9 mls). Pull the plunger to 5.0 mls for addition of the sample extract. Add the volume of methanol extract determined from screening (recommend a maximum volume of 100 ul).

9.5.2.6 Add bromofluorobenzene to the diluted extract by spiking the surrogate directly into the sample syringe. Inject the sample into the purging chamber.

9.5.2.7 Proceed with the analysis as in 9.5.1.9-9.5.1.14. Analyze all reagent blanks and QC samples on the same instrument as that used for the samples. The reagent blank should contain 100 ul of the methanol used to extract the samples (or a volume equal to the largest amount of extract purged).

9.5.2.8 If the responses exceed the calibration or linear range of the systems, repeat the analysis using a smaller aliquot of methanol extract.

9.6 Calculations:

9.6.1 GRO Calibration: The concentration of Gasoline Range Organics in the sample is determined from a summation of the total peak area for all chromatographic peaks eluting from methyl-tertiary-butylether through naphthalene, inclusive, using the calibration curve. (Using a "baseline to baseline" integration as opposed to a "valley to valley" integration.) Refer to Section 9.3 (Retention Time Windows and Quantitation).

Quantitation may be based on an average response from the calibration curve or on a linear regression equation derived from the curve.

Linear regression: From the calibration standards GC responses, R, and their known concentrations, C in ug/L, the following linear equation may be derived
[R is plotted on the y axis; C is plotted on the x axis]:

$R = mC + b$; which can be rearranged to $C = (R - b)/(m)$.

Using the slope (m) and the intercept (b) from this equation the concentration of the sample can be calculated from the following equations:

Water Samples

$Cs = (Rs - b)(D)/(m)$

Soil Samples

$Cs = [(Rs-b)(D)(Vt)(K)]/[(Vp)(W)(m)]$

Where:

Cs = Concentration of sample in ug/L for waters and mg/kg on a dry weight basis for soils. (Note: Wet weight basis can be used, if client wants results on that basis.)

m = slope of the calibration curve

Rs = GC response of sample in the GRO retention time window

b = intercept of calibration curve

D = dilution factor if water sample or soil extract was diluted

Vp = volume of soil extract purged (units must be the same as those used for Vt)

Vt = total volume of soil extract

$K = 5 \times 10^{-6}$ L mg/ug (this constant adjusts for both conversion from ug/kg to mg/kg and for the dilution of the volume of extract purged up to the 5 mls used for purging)

W = total dry weight of soil sample in kg. (This weight can be the wet weight if the client requests results on a wet weight basis).

9.6.2 Blank areas may not be subtracted from sample areas. Chromatographic baseline rises due to temperature programming may be corrected for by using baseline correction. The baseline correction may be performed by the most convenient method that the data handling system allows.

9.6.3 If a water blank concentration (this does not include trip blanks) exceeds 25 ug/L (or minimum reporting level, if lower), all water samples associated with this blank (samples run since the last blank that was below 25 ug/L) must be rerun.

9.6.4 If a methanol blank concentration (this does not include trip blanks) exceeds 2.5 mg/L, all soil samples associated with this blank (samples that have concentrations greater than 2.5 mg/kg run since the last blank that was below 2.5 mg/L) must be rerun.
Note: This blank level is equivalent to 50 ug/L in the water sample prepared by spiking 100 ul of the methanol blank into 5 ml of water. This is also equivalent to 2.5 mg/kg in soil.

9.6.5 To ensure that peaks outside the GRO window are not missed, run the chromatogram out 5 minutes past the last component in the GRO component standard. All significant peaks (and baseline rises) outside the window should be qualitatively assessed and reported.

10. Quality Control

10.1 The analyst must make an initial demonstration of the ability to generate acceptable accuracy and precision with this method by successful analysis of the following:

10.1.1 Replicate Commercial Gasoline Spikes in Water: Analysis of 7 replicates at a concentration of 50 ug/L (in water) with an accuracy falling between 60% and 140% of the known concentration with a precision of 20% or less.

10.1.2 Replicate Commercial Gasoline Spikes in Soil: Analysis of 7 replicates at a concentration of 5 mg/kg with an accuracy between 60% and 140% of the known concentration and the precision should be within 20%. Soil spikes should be prepared and analyzed as described in Section 10.3.

10.2 For every 20 samples analyzed the lab must analyze a set of duplicate Gasoline component Spikes in water. The duplicate spikes must be run through the method in the same manner as samples. The accuracy of the two water spikes must be within 40% of the known concentration and the percent relative difference between the two values must be 20% or less.

10.3 With every analytical sequence containing soil samples, the lab must analyze one Gasoline Component Spike in clean sand or soil. The spike amount should fall in the linear range of the detector. The spike recovery must be between 60% and 140%. If soil samples are methanol preserved in the field, soil spikes must be prepared at least 24 hours prior to extraction, held at 4C, and analyzed with a batch of samples. If soils are extracted in the lab, the soil spike should be prepared at the time of the extraction and analyzed along with the samples.

10.4 A water blank (containing purge-and-trap surrogate) must be run with every analytical sequence containing water samples, utilizing the same water used to prepare standards and make dilutions. The amount of material in the blank should not exceed one-half of the minimum reporting level.

10.5 A reagent methanol blank (containing both the purge-and-trap surrogate and the extraction surrogate) must be run with each analytical sequence containing soil samples, utilizing the same water used to prepare standards and dilute extracts and a methanol spike of 100 ul (or largest amount of extract used). The amount of material in the blank should not exceed one-half of the minimum reporting level.

10.6 Calibration requirements

10.6.1 When linear regression analysis is used for calculations the correlation coefficient must be at least .99.

10.6.2 When average Rf is used for calculations, the relative standard deviation of the Rf's must not exceed 20%.

10.6.3 A Quality Control Check Standard (obtained from a source independent of the calibration standards) should be analyzed concurrent with the calibration standards in order to confirm the validity of the calibration curve. The QC check should fall within 20% of the expected value using the calibration data.

10.6.4 The calibration curve must be verified with each analytical sequence by running a mid-point calibration standard. The response must fall within 20% of the expected response.

10.7 If any of the criteria above are not met, the problem must be corrected before further samples are analyzed. Any samples run between the last QC samples that meet the criteria and those that do not meet the criteria should be rerun. If reanalysis is not possible, the data must be flagged.

10.8 Laboratory Spiked Duplicates must be run at a frequency of 10% **Alternatively duplicate samples and spiked samples can be substituted for the laboratory spiked duplicates at a frequency of 10%. Care must be taken to ensure that the samples are homogeneous before analyzing duplicates and spikes.**

10.9 One methanol field blank must accompany each sampling event (for each site and each day that samples are collected and preserved in the field).

10.10 Trip blanks, field blanks, field duplicates and/or matrix spikes may be required for specific sampling programs.

10.11 Water blanks should be run after samples suspected of being highly concentrated to prevent carryover.

10.12 It is recommended that an acceptance criteria be established for recoveries of surrogates. Collect recoveries from 30 samples where no interference is suspected and calculate the mean recovery (X) and standard deviation (S). The acceptance limits for samples not exhibiting matrix interference will be X-3S to X+3S. The warning limits will be X-2S to X+2S. Plotting the surrogate recoveries on a control chart will make checking recoveries easier and is highly recommended.

If surrogate recovery is outside of the established limits, verify calculations, dilutions, and standard solutions. Verify instrument performance, including checking for leaks and purge problems if the recovery is low. Low recovery may be due to the sample matrix. The analysis should be repeated, if the recovery is less than 50% or, if the analyses cannot be repeated, the data should be flagged.

High recoveries may be due to coeluting matrix interference. Surrogate recoveries may be reported as "masked" in high level samples exhibiting matrix interference. Additionally, the extraction surrogate may be reported as "diluted out" in high level soil samples that must be diluted for analysis. These samples do not need to be rerun solely to try to bring surrogate recovery into acceptance limits.

10.13 The laboratory should analyze a mid-range certified gasoline composite in water on a weekly basis.

11. Method Performance

11.1 Detection limit for water

The laboratory must achieve an MDL of 10 ug/L or less using a commercial gasoline mixture spiked into blank water and calculated against the ten component standard.

11.2 Detection limit for soil

The laboratory must achieve an MDL of 2.5 mg/kg or less using a commercial gasoline mixture spiked onto a blank sand and calculated against the ten component GRO standard.

12. References

12.1.Wisconsin DNR Modified GRO , July 1993

12.2. American Petroleum Institute " Method for Determination of Gasoline Range Organics", August 1993.

12.3.USEPA SW 846, 3 rd edition, Methods 5030, 8000, 8015 and 8020.

TABLE 1
PURGE AND TRAP OPERATING PARAMETERS

Recommended conditions for suggested trap from Section 6.1.4.2	
Purge gas	Nitrogen or Helium
Purge gas flow rate (ml/min)	40
Purge time (min)	11.0 ± 0.1
Purge temperature (°C)	35°C or less
Desorb temperature (°C)	250°C

TABLE 2
GASOLINE COMPONENT STANDARD AND CONCENTRATIONS

Component	Concentration, ug/ml
Methyl-t-butylether	1000
Benzene	1000
Toluene	1000
Ethylbenzene	1000
m-Xylene	1000
p-Xylene	1000
o-Xylene	1000
1,2,4-Trimethylbenzene	1000
1,3,5-Trimethylbenzene	1000
Naphthalene	1000
Total	10,000